



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: H01L 29/43, H01L 21/441	A1	(11) International Publication Number: WO 00/11721
		(43) International Publication Date: 02 March 2000 (02.03.2000)

(21) International Application Number: PCT/US99/16719	Published
(22) International Filing Date: 18 August 1999 (18.08.1999)	
(30) Priority Data:	
09/137,083	20 August 1998 (20.08.1998) US
09/137,084	20 August 1998 (20.08.1998) US
09/137,085	20 August 1998 (20.08.1998) US
09/137,086	20 August 1998 (20.08.1998) US
09/137,087	20 August 1998 (20.08.1998) US
09/137,088	20 August 1998 (20.08.1998) US
09/137,089	20 August 1998 (20.08.1998) US
09/215,127	18 December 1998 (18.12.1998) US
09/215,128	18 December 1998 (18.12.1998) US
(60) Parent Application or Grant	
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(54) Title: ELECTRONIC DEVICES WITH BARRIER FILM AND PROCESS FOR MAKING SAME

(54) Titre: DISPOSITIFS ELECTRONIQUES POURVUS DE FILMS BARRIERES ET PROCEDE DE FABRICATION

(57) Abstract

A semiconductor device having a barrier film (47) comprising an extremely thin film formed of one or more monolayers each comprised of a two-dimensional array of metal atoms. In one exemplary aspect, the barrier film (47, 49) is used for preventing the diffusion of atoms of another material (45) such as copper conductor, into a substrate (46), such as a semiconducting material or an insulating material, and an oxide layer (48). Methods for making the barrier film (47) in a semiconductor device are also covered. The extremely thin barrier film (47, 49) makes possible a significant increase in the component density and a corresponding reduction in the number of layers in large scale integrated circuits, as well as improved performance.

(57) Abrégé

Ce dispositif à semi-conducteurs est pourvu d'un film barrière (47), constitué d'une pellicule extrêmement mince formée d'une monocouche, sinon de plusieurs, faites, chacune, d'un réseau bi-dimensionnel d'atomes de métal. Dans un mode de réalisation, donné à titre d'exemple, on utilise le film barrière (47, 49) pour empêcher la diffusion d'atomes d'une autre matière (45), un conducteur en cuivre notamment, dans un substrat (46), tels qu'un matériau semi-conducteur ou isolant, et dans une couche d'oxyde (48). L'invention a également trait à des procédés de fabrication de ce film barrière (47) dans un dispositif à semi-conducteurs. La présence de ce film barrière extrêmement mince (24, 54) permet d'accroître la densité du composant et de réduire, de façon corollaire, le nombre de couches dans des circuits intégrés de grande taille ainsi que d'améliorer les caractéristiques de fonctionnement.

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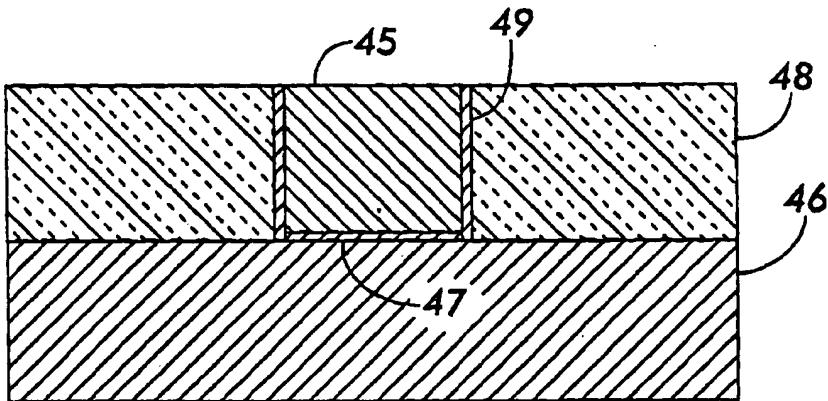
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(51) International Patent Classification 6 : H01L 29/43, 21/441	A1	(11) International Publication Number: WO 00/11721 (43) International Publication Date: 2 March 2000 (02.03.00)																											
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 (22) International Filing Date: 18 August 1999 (18.08.99)		 (81) Designated States: CA, CN, IL, JP, KR, MX, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).																											
 (30) Priority Data: <table><tr><td>09/137,083</td><td>20 August 1998 (20.08.98)</td><td>US</td></tr><tr><td>09/137,084</td><td>20 August 1998 (20.08.98)</td><td>US</td></tr><tr><td>09/137,085</td><td>20 August 1998 (20.08.98)</td><td>US</td></tr><tr><td>09/137,086</td><td>20 August 1998 (20.08.98)</td><td>US</td></tr><tr><td>09/137,087</td><td>20 August 1998 (20.08.98)</td><td>US</td></tr><tr><td>09/137,088</td><td>20 August 1998 (20.08.98)</td><td>US</td></tr><tr><td>09/137,089</td><td>20 August 1998 (20.08.98)</td><td>US</td></tr><tr><td>09/215,127</td><td>18 December 1998 (18.12.98)</td><td>US</td></tr><tr><td>09/215,128</td><td>18 December 1998 (18.12.98)</td><td>US</td></tr></table>			09/137,083	20 August 1998 (20.08.98)	US	09/137,084	20 August 1998 (20.08.98)	US	09/137,085	20 August 1998 (20.08.98)	US	09/137,086	20 August 1998 (20.08.98)	US	09/137,087	20 August 1998 (20.08.98)	US	09/137,088	20 August 1998 (20.08.98)	US	09/137,089	20 August 1998 (20.08.98)	US	09/215,127	18 December 1998 (18.12.98)	US	09/215,128	18 December 1998 (18.12.98)	US
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A semiconductor device having a barrier film (47) comprising an extremely thin film formed of one or more monolayers each comprised of a two-dimensional array of metal atoms. In one exemplary aspect, the barrier film (47, 49) is used for preventing the diffusion of atoms of another material (45) such as copper conductor, into a substrate (46), such as a semiconducting material or an insulating material, and an oxide layer (48). Methods for making the barrier film (47) in a semiconductor device are also covered. The extremely thin barrier film (47, 49) makes possible a significant increase in the component density and a corresponding reduction in the number of layers in large scale integrated circuits, as well as improved performance.

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Description

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DescriptionELECTRONIC DEVICES WITH BARRIER FILM
AND PROCESS FOR MAKING SAME

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Statement of Government Interest

15 The invention described herein may be manufactured and used by or for the Government of the United States of America for Governmental purposes without the payment of any royalties
20 5 thereon or therefor.

Technical Field

25 This invention relates generally to the fabrication of electronic devices, and particularly to a novel barrier film for electronic and electro-optic materials.

10 Background Art

30 Integrated circuits (ICs) are composed of many millions (sometimes billions) of components such as transistors, resistors, and capacitors. These individual components are laid out in a two dimensional array on a substrate such as
35 15 silicon or gallium arsenide. The two dimensional arrays are often stacked one on top of another to form a three
40 45 dimensional IC. As in any circuit, these components, and the several layers, must be connected to one another electrically. Interconnection on the two dimensional surfaces is
45 20 accomplished by depositing strips of metal that act as connecting "wires." Likewise, the layers are interconnected by metal plugs deposited in via holes made between layers.
50 55 These steps in the manufacturing process are commonly referred

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to as "metallization."

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Generally, silicon is the substrate material of choice, aluminum is the metal of choice for two dimensional IC metallization, and tungsten is the metal of choice for filling via holes for multiple layer interconnection. Silicon is preferred because it is cheap and abundant. Aluminum and tungsten are chosen because they have adequate electrical conductivity and they can be made not to diffuse into the substrate during the many annealing operations inherent in the IC manufacturing process.

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Because the electrical conductivity of aluminum and tungsten is limited, the "wires" and plugs must be made thick enough to ensure minimal resistance to electric current between components and between layers. The large size of these conductors has recently become an issue for IC designers and fabricators interested in placing a greater density of circuit elements on an IC. In order to achieve greater performance from ICs, the lateral dimensions of the circuit elements must be reduced. This reduction in IC element size has two detrimental effects on the resulting IC. First, it increases the resistance of the metal interconnects. Second, it increases the aspect ratio of the via holes, making them more difficult to fill with the metallic material. Incomplete filling of the via holes exacerbates the problem of high resistance. Today, there is often not enough space in the lateral direction on an IC chip to accommodate large aluminum conductors. Additionally, the size of the via holes, when

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5 filled with tungsten, limits the number of levels in the IC to
no more than five.

10 Copper, which is a much better conductor of electricity
than aluminum, is available as an alternative metallization
5 material. Because of copper's greater electrical
conductivity, copper imposes less resistance to the flow of
15 electrons than aluminum or tungsten conductors having
equivalent dimensions. The increasing density of components
on today's ICs requires the smaller sized conductors that are
20 only achievable by the use of highly conductive metallization
10 materials.

Unfortunately, copper has one notable problem. It has a tendency to diffuse into silicon at elevated temperatures.

This has precluded copper as a metallization candidate because
30 15 ICs must be annealed several times during the manufacturing
process. In order for copper metallization to be feasible, a
technique must be developed that will prevent the diffusion of
35 copper into silicon. Among the possible solutions currently
under development within the semiconductor industry the most
40 20 prevalent is the use of nitrides of the transition metals
titanium and tungsten. The thickness of the metal-nitride
layer required to stop copper diffusion into silicon
45 effectively is in the range of tens to hundreds of nanometers,
or hundreds to thousands of Angstroms (Å).

25 The problem of diffusion exists not only in the case of
50 copper metallization on silicon, but also in the case of
copper metallization on other single- and polycrystalline

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5 semiconductor substrate materials such as gallium arsenide,
silicon carbide, germanium, and so forth. Copper diffusion
10 into insulating materials such as SiO₂, can also result in short
circuits, especially in dense arrays of IC components.

15 5 Diffusion is also a problem with other high conductivity
metallization materials such as gold, silver, and platinum.

20 An object of this invention is to provide a barrier film
which is extremely thin, yet permits metallization using
copper and other high conductivity metallic conductors which
25 10 would otherwise have a tendency to diffuse into a substrate
formed of a semiconducting or insulating material.

25 It is also an object of the invention to improve
electronic and electro-optic devices by making it possible to
achieve one or more of the following desirable
30 15 characteristics: increased component density in large scale
integration, reduced heat dissipation, increased speed of
operation, and a decreased number of layers.

35 Still another object is to provide a procedure for
forming an extremely thin diffusion barrier, which produces
40 20 consistent results rapidly and reliably, and which is not
highly dependent upon the accurate maintenance of operating
conditions such as time and temperature.

45 Still another object is to provide a process for forming
an extremely thin diffusion barrier which eliminates voids and
50 25 mechanical stresses that can have detrimental effects on the
substrate, the diffusion barrier, or the metallization layer.

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Disclosure of the Invention

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In accordance with this invention, a semiconductor device is fabricated by forming, on a surface of a substrate material, a barrier film having a monolayer of metal atoms immediately adjacent the surface of the substrate material. In one aspect, 5 a metallic conductor, which has a tendency to diffuse into the substrate material, is then deposited onto the barrier film.

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Metallic conductors which have a tendency to diffuse into substrates of semiconductor or insulating materials include,

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10 for example, pure copper, copper alloys (e.g., Cu-Al, Cu-Si-Al), copper doped with a dopant (e.g., aluminum) that impedes electromigration, gold, silver, or platinum. For purposes of 25 this invention, a "monolayer" is understood to refer to a two-dimensional array of atoms having the thickness of one atomic layer; although the monolayer may have minuscule defects such 30 as minute portions with a thickness that exceeds one atomic layer and/or minute portions that are voids, the average

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35 thickness nonetheless essentially is an atomic layer providing essentially complete coverage of the directly underlying

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40 substrate surface regions. The monolayer, which is extremely thin by definition, serves as a barrier film, inhibiting diffusion of the metallic conductor into the substrate 45 material. For purposes of this application, the material upon which the monolayer of atoms is formed is often generally

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50 referred to herein as a "substrate" for such formation, and it will be appreciated that the term "substrate" as used herein can encompass a bulk wafer or, alternatively, a layer that is

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5 grown, deposited, formed or bonded upon another body. The
10 present invention is especially concerned with substrates that
are semiconductor or insulating materials.

10 In one preferred method of this invention, a monolayer is
5 produced by depositing a metal halide upon a surface of a
15 semiconducting or insulating substrate material where it first
reacts with the substrate material and dissociates, releasing
gaseous by-products formed of substrate atoms and halogen atoms
20 of the precursor compound. This reaction is self-limiting
10 resulting in formation of a monolayer of metal atoms on the
substrate that thereafter enables a homoepitaxial film formed
25 of the metal halide molecules to form thereon as the deposition
process proceeds. This deposition operation can be carried out
by various methods, but is preferably carried out by molecular
30 beam epitaxy, or alternatively by r.f. sputtering. At this
15 juncture, a temporary heteroepitaxial film has been formed on
the substrate where the diffusion barrier is ultimately
35 desired. Then, in a second stage of the procedure, the
temporary heteroepitaxial film is subjected to a selective
20 removal procedure, whereby the homoepitaxial portion of the
40 deposited film having the halogen constituents is selectively
eliminated while the monolayer of metal atoms remains behind
attached to the surface of the substrate material. The removal
45 procedure preferably is an annealing operation. Alternatively,
25 chemical etching which is selective to remove the homoepitaxial
portion of the deposited film while leaving the monolayer of
50 metal atoms also can be used. In any event, the metal atom

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5 monolayer strongly adheres to the substrate material, and is
not adversely affected by extended annealing times, high
10 annealing temperatures, or chemical etching conditions.

10 The precursor compound preferably comprises a metal
15 halide, e.g., a barium, strontium, cesium or rubidium- halide
salt. The thickness of the monolayer basically corresponds to
the diameter of the metal atom constituent(s) of the monolayer.
Metal atoms of barium, strontium, cesium, rubidium, and so
20 forth have a thickness (i.e., the diameter of the largest
10 electron orbital) of less than 5 Å, so it can be appreciated
that an extremely thin diffusion barrier layer is achieved by
this invention. The semiconducting substrate materials that can
25 be processed according to this invention include mono- or
polycrystalline, doped or undoped, semiconductors, such as
30 15 silicon, germanium, indium phosphide, gallium arsenide, silicon
carbide, gallium nitride, aluminum nitride, indium antinomide,
lead telluride, cadmium telluride, mercury-cadmium telluride,
35 lead selenide, lead sulfide, tertiary combinations of these
materials, and so forth. The insulating substrate materials
40 20 that can be processed according to this invention include doped
or undoped silicon oxides (e.g., silicon dioxide), silicon
nitride, phosphosilicate glass (PSG), borophosphosilicate glass
(BPSG), barium fluoride, strontium fluoride, calcium fluoride,
45 and so forth.

50 25 In a further embodiment of this invention, a multiplicity
of monolayers are formed contiguous with each other upon the
substrate surface. This embodiment can become advantageous such

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as where a substrate is involved having a relatively greater
surface roughness and it is necessary to account for any
discontinuities in the surface profile by sufficiently
building-up the diffusion layer to blanket the surface

5 topography presented and provide complete coverage. To build-up
multiple monolayers, one stacked upon the other, MBE deposition
can be used to sequentially deposit additional monolayers of
metal atoms using an elemental source of the metal. In this
way, a diffusion barrier film thickness can be assembled up to
10 any desired thickness, but preferably is maintained at or below
not more than 100 Å, more preferably not more than 20 Å to
meet the primary objective of providing an extremely thin yet
25 effective diffusion barrier.

As can be appreciated, a semiconductor device is obtained
30 by this invention in which a monolayer or several monolayers of
metal atoms separates a metallic conductor from other materials
in the device, such as semiconductor or insulating materials,
35 in which the extremely thin diffusion barrier film serves as an
effective barrier preventing atoms of the metallic conductor
20 from diffusing into such other materials and either impairing
40 the device or rendering it totally inoperative.

Various other objects, details and advantages of the
invention will be apparent from the following detailed
45 description when read in conjunction with the drawings.

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Brief Description of Drawings

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FIG. 1 is a schematic cross-section depicting diffusion of copper into a silicon substrate, where no diffusion barrier is present;

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FIG. 2 is a graph illustrating the projected requirement in diffusion barrier thickness by the Semiconductor Industry Association;

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FIG. 3 is a schematic cross-section depicting the effect of a diffusion barrier in accordance with the invention;

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FIG. 4 is a schematic diagram illustrating the process of deposition of a diffusion barrier precursor compound, and a metallization layer, onto a substrate by molecular beam epitaxy;

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FIGS. 5A-E is a schematical illustration showing the interfacial structure of the diffusion barrier on an atomic level as it is being formed on a semiconductor substrate after various process steps according to an inventive process;

35

FIG. 6 is a schematic diagram illustrating the process of deposition of a diffusion barrier precursor compound onto a substrate by r.f. sputtering; and

40

FIG. 7A is a schematical illustration showing the interfacial structure of the barrier film on an atomic level where the barrier film is comprised of a plurality of contiguous monolayers, while FIG. 7B shows another embodiment of the invention where the barrier film is a composite monolayer formed of different types of metal atoms, and FIG. 7C shows yet another embodiment where the barrier film is

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5 comprised of a plurality of contiguous monolayers in which
different monolayers thereof are formed of different types of
10 metal atoms.

10 FIG. 8 is a schematic cross-sectional view showing a
5 diffusion barrier in accordance with the invention preventing
15 diffusion of a copper plug into silicon substrate and into a
silicon dioxide insulating layer overlying the substrate.

20 Best Mode for Carrying Out the Invention

10 FIG. 1 illustrates a typical attempt at copper
metallization of a silicon semiconductor substrate 10. The
25 substrate, which is made up of silicon atoms 12, has two
laterally delineated copper interconnect strips 14 deposited on
its surface. In the annealing process, copper atoms 16 tend to
30 diffuse into the substrate, impairing its semiconducting
15 properties, and usually rendering it totally inoperative, by
effectively creating an electrical short circuit. Similar
35 diffusion occurs at an interface between a copper conductor and
a SiO₂ insulating layer, for example in the case in which an
20 attempt is made to deposit a conducting copper plug in a via
40 hole in the SiO₂ insulating layer. Diffusion of copper atoms
into the SiO₂ insulating layer impairs its effectiveness as an
insulator and may have a serious adverse effect on the
45 properties of the device.

25 As mentioned above, various attempts have been made to
achieve a diffusion barrier to permit the use of copper
50 conductors in semiconductor devices. The most attention so far

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has been given to the use of nitrides of tungsten and titanium. Various other diffusion barrier materials, for example tantalum nitride, have also been tried. As shown in FIG. 2, which is based on published Semiconductor Industry Association data, 10 presently achievable diffusion barrier thicknesses are only in the 200-250 Å range for tantalum nitride, although thicknesses 15 smaller than that are expected to be pursued by the industry in the upcoming years.

20 This invention provides an effective diffusion barrier

10 having a thickness well below 100 Å, and below 5 Å in one exemplary embodiment, which is far below the minimum thickness 25 projected by the industry data depicted in FIG. 2. The extremely thin diffusion barrier layers achievable by this invention potentially could be useable long after alternative 30 technologies become obsolete.

Referring now to FIG. 3, a portion of an integrated 35 circuit is schematically illustrated on an atomic level that comprises a silicon substrate 18 made up of silicon atoms 20, and having laterally delineated copper interconnect strips 22.

40 At the upper surface of the silicon substrate 18, a monolayer of barium (Ba) atoms 24 is interposed between the conductor strips 22 and the surface of the substrate 18 and effectively prevents diffusion of the copper atoms into the silicon. The 45 layer of Ba atoms need only have a thickness of one atomic 50 layer, i.e., a monolayer of approximately 5×10^{-10} meters (5Å) in thickness, in order to provide the desired barrier to diffusion of the conductor into the adjoining substrate. The

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barium layer depicted in Fig. 3 illustrates the situation in
which a single monolayer of barium is provided. The extremely
small thickness of the diffusion barrier contributes to the
reduction in both thickness and the lateral dimensions of the
integrated circuit layer, and the ability to use copper
interconnects and other conductor materials otherwise
predisposed to creating diffusion problems (e.g., Au, Ag, Pt)
instead of aluminum interconnects. As such, the present
invention represents a remarkable breakthrough in the field.

10 As will become apparent from the following description, in
one mode of this invention, a diffusion barrier comprised of
metal atoms and having a thickness of not more than
approximately 5Å is achievable by depositing a metal halide
precursor compound on a semiconductor or insulating substrate
so as to form a temporary heteroepitaxial film thereon. Then,
the resulting temporary heteroepitaxial film created by the
metal halide and the substrate surface is subjected to a post-
growth anneal or chemical etching in which all of the temporary
heteroepitaxial film is eliminated by removal from the
substrate except for an atomic layer of the metal component,
i.e., a monolayer. This residual monolayer of metal atoms
disposed in contact with the substrate surface provides a
diffusion barrier to conductor materials.

45 One suitable approach for depositing the metal halide used
as a precursor compound for forming the diffusion barrier layer
is molecular beam epitaxy (MBE), such as depicted in FIG. 4. A
substrate 26, e.g., a silicon wafer, is supported on a rotating

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holder 28 within a conventional MBE deposition chamber 30. The deposition chamber is illustrated in simplified form. Not shown are provisions for raising the temperature of the substrate to annealing temperatures and for evacuating the 10 chamber. Also not shown is a conventional Reflective High Energy Electron Diffraction (RHEED) diagnostic system directed 15 toward the substrate 26.

A diffusion barrier precursor compound effusion cell, for 20 example a barium fluoride, strontium fluoride or the like 10 effusion cell, is provided at 32, and has a shutter 33. A shutter 35 is also provided for the silicon wafer 26. An 25 electron beam source for the metallization layer, e.g., copper, is shown at 34.

In the operation of the MBE deposition apparatus of FIG. 30 15, the substrate 26 is placed inside the chamber 30 and positioned by rotatable holder 28 and the chamber 30 is evacuated, using ion pumps and liquid nitrogen trapping to 35 achieve a high vacuum. The substrate 26 is vacuum annealed to remove any passivation layer by deoxidation, for example 20 silicon dioxide in the case of a silicon wafer.

The temperature of the substrate 26 is then reduced to a 40 suitable deposition temperature, and the effusion cell 32 is heated while the substrate 26 is mechanically rotated. The 45 electron beam of a RHEED diagnostic system is focused onto the 25 substrate 26 and the RHEED pattern is monitored. When the 50 RHEED pattern corresponding to the single crystal substrate surface appears (indicating complete removal of the passivation

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layer) on the RHEED screen, the shutters 35 and 33 in front of
the substrate holder 28 and the effusion cell 32, respectively,
are opened to allow precursor molecules to impinge on the
10 substrate surface 29. Deposition of the precursor 27 onto the
5 silicon surface 29 begins, and is allowed to continue until the
15 single crystal silicon RHEED pattern disappears and is replaced
by a pattern corresponding to a single crystal layer of the
precursor compound. Deposition is halted by closing the
20 substrate and effusion source shutters 35 and 33, respectively.

10 By this juncture, a temporary heteroepitaxial film derived from
the precursor molecules is situated on the substrate surface
25 29, although the nature of the interface is more complicated as
will become apparent from later descriptions herein.

During the deposition of the precursor 27 on the substrate
30 26, the substrate 26 should be at a temperature in the range
15 from approximately 500°C to 800°C, and ideally at approximately
750°C, though the temperature will vary depending on the
35 particular substrate and the processing tool. The pressure
within the deposition chamber 30 should be 10⁻⁸ mbar or less,
20 more preferably 10⁻⁹ mbar or less, and still more preferably
40 10⁻¹⁰ mbar or less, in the case of depositing a metal halide on
a silicon substrate. The time required to achieve adequate
45 deposition of the precursor sufficient to form the temporary
heteroepitaxial film on the substrate is typically one or two
25 minutes, but is not limited thereto.

Following the deposition on the substrate of the temporary
50 heteroepitaxial film derived from the precursor compound, the

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temperature of the substrate is raised to cause precursor molecules to detach from the temporary heteroepitaxial film on the substrate. In the case of BaF₂, barium atoms adjacent to the substrate remain tightly adhered thereto as a two-dimensional monolayer, while fluorine atoms (as bonded to other barium atoms) in the temporary heteroepitaxial film are effectively re-evaporated in the form of barium fluoride and eliminated from the temporary heteroepitaxial film. This will cause the RHEED pattern to change in appearance. Specifically, the "reappearance" of a RHEED pattern similar to that for the single crystal substrate confirms that the precursor molecules have been evaporated. The substrate temperature at which the detachment of the precursor molecules with the halogen atoms from the temporary heteroepitaxial film takes place during the post-growth anneal step is not necessarily limited, but should be in the vicinity of 750°C to 1000°C, preferably 800°C. The monolayer of metal atoms which remains on the substrate serves as the diffusion barrier between the substrate and any metallization layer subsequently deposited upon it. The metallization layer can be deposited by any of various standard microelectronic metallization methods, and, in this embodiment, it can be conveniently deposited while the substrate is still in the MBE chamber by operation of the electron beam source.

The crystallographic and chemical characterization of the aforesaid temporary heteroepitaxial film, and the effect of treatments thereof according to this invention to form a diffusion barrier film on the substrate, are now discussed in

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5 greater detail. Based on X-ray photoelectron spectroscopy (XPS) and heavy ion backscattering spectroscopy (HIBS) analyses of
10 the precursor compound/substrate surface interfacial chemistry,
the formation of an ultra-thin metal monoatomic layer
5 (monolayer) on the substrate is considered to proceed by a
15 multi-stage process, which is schematically illustrated in FIGS. 5A-E. XPS and HIBS analysis measurements referred to
herein can be performed using generally available equipment and
20 analyses protocol understood and implementable by one skilled
10 in the art.

As schematically illustrated in FIG. 5A, BaF₂ molecules 50
25 are directed and impinged onto the surface 51 of a silicon
substrate 52, such as by MBE deposition. For FIGS. 5A-E, BaF₂,
is used to illustrate the metal halide, and silicon is used to
30 15 illustrate the (semiconductor) substrate, although other
materials can be used as indicated elsewhere herein.

Ideally, the silicon surface 51 to be used as the
35 deposition substrate has a highly planar, smooth surface to
minimize the coating thickness needed to provide complete
20 coverage thereof. Deoxidation annealing, chemical-mechanical-
planarization (CMP) polishing or ion milling can be used in a
40 pretreatment of the silicon surface prior to deposition of the
diffusion barrier to enhance the planarity and smoothness of
45 silicon surface, if necessary. On the other hand, as will be
25 described below, the inventive process itself provides some
measure of *in situ* planarization of the silicon surface during
50 MBE deposition.

5 -17-

In any event, in the first step, the BaF₂ molecules react with silicon atoms 51a, 51b, 51c, and so forth, at the surface 51 of the silicon substrate 52. The Ba-F and silicon-silicon bonds at the surface of the silicon substrate are broken. As 10 schematically shown in FIG. 5B, the free silicon and fluorine atoms at the vicinity of the interface where the barium 15 fluoride molecules are contacting the silicon surface 51 then combine to form volatile silicon-fluoride compounds (SiF_y) 53 which escapes from the silicon substrate surface 51, and it is 20 extracted from the MBE chamber via vacuum. Although FIG. 5B depicts compound 53 as two halide atoms (white circles) bonded 25 to a common metal atom (darkened circle), it will be understood that this illustrative only because other gaseous metal-halides may be generated, such as tetrahalides of silicon where the 30 substrate 52 is silicon. By comparison, if the substrate 52 instead is GaAs, the escaping gas 53 would be GaF. This etching-like effect upon the surface silicon atoms serves to 35 effectively smoothen the silicon surface. In any event, as illustrated in FIG. 5B, the barium atoms left behind bond with 40 dangling bonds of the surface silicon atoms, forming a monoatomic layer 54 of metal atoms, i.e., a metal monolayer of 45 barium atoms. This deposition step proceeds for a sufficient duration of time to form a continuous layer of barium atoms across the surface of the silicon substrate without leaving any 50 bare spots.

As illustrated in FIG. 5C, once complete coverage of the silicon substrate 52 with barium atoms 54 is achieved, barium

5 -18-

fluoride 50 deposition via MBE is continued from a molecular beam. As illustrated in FIG. 5D, this subsequently introduced barium fluoride adheres to the barium monolayer 54 and grows epitaxially thereon to form a temporary homoepitaxial film portion 55. The amount of subsequent deposition of epitaxial barium fluoride on the barium monolayer is allowed to be enough to provide a safety measure which ensures complete substrate coverage with a monolayer of barium atoms. In this way a heteroepitaxial film 56 is formed on the substrate surface 51 comprising a monolayer 54 of metal (e.g., Ba) atoms as an interaction regime attached directly to the substrate surface 51 and a homoepitaxial regime 55 comprised of oriented molecular metal halide (e.g., barium fluoride) formed, in turn, on the monolayer 54. The homoepitaxial regime 55 of BaF₂ of the temporary heteroepitaxial film 56 is (100)-oriented on silicon (100), and (111)-oriented when the substrate is silicon (111), GaAs (100), or GaAs (111).

XPS measurements have confirmed that barium atoms have the two above-mentioned different chemical states, i.e., the interaction (metal monolayer) and the homoepitaxial regimes, in the temporary film present at this stage of processing. The relative abundance of these two states has also been determined by XPS. The number of barium atoms in each state is determinable by normalizing integrated XPS peak intensities to HIBS measurements of the total number of barium atoms on the surface. The results of these analyses confirm that BaF₂ first reacts with the silicon surface during initial MBE deposition

5 -19-

5 at the silicon surface and dissociates, releasing a gaseous
10 silicon-fluorine compound. This reaction is self-limiting,
resulting in a barium monolayer that enables subsequent BaF₂
15 molecules to form an epitaxial (111)-oriented film on the
5 silicon surface. Then, a post-growth anneal affects evaporation
of the barium fluoride deposited on the monolayer.

That is, as illustrated in FIG. 5E, in a second stage of
20 this inventive procedure, which is conducted after the MBE
deposition of the metal halides on a substrate to form the
10 temporary heteroepitaxial film 56 shown in FIG. 5D,
a vacuum anneal is performed to cause evaporation of barium
25 fluoride 57 from the temporary heteroepitaxial film such that
the barium fluoride content found in the homoepitaxial portion
thereof (feature 55 in FIG. 5D) is completely removed back to
30 the monolayer 54 of barium atoms attached to the silicon
surface 51. Alternatively, the homoepitaxial portion 55 of the
temporary heteroepitaxial film can be removed by etching (e.g.,
35 chemical etching) which is selective between the homoepitaxial
portion 55 and the monolayer portion 54 such that the former
20 can be removed while leaving the latter intact.

40 In any event, prior to performing the post-growth anneal
(or etching) to remove the homoepitaxial portion 55 of the
temporarily heteroepitaxial film, there is no practical limit on
45 how thick the overdeposit of barium fluoride can be that is
25 formed over the barium monolayer. However, it will be
appreciated that the thicker the deposited barium fluoride
50 layer(s) of the homoepitaxial portion of the temporary film is

5 -20-

made to be, the longer the post-growth anneal time that will be
necessary to decompose the deposited thickness of barium
fluoride molecules back to the monolayer of barium atoms left
attached to the substrate surface.

5 The MBE deposition of the temporary heteroepitaxial film
and the post-growth anneal can be performed in the same
15 processing chamber without breaking the vacuum between the two
procedures. Alternatively, the MBE deposition can be performed
20 in a first processing tool, after which the vacuum is broken,
10 and the workpiece is then transferred to another processing
tool for separately performing the post-growth anneal at which
time the substrate is heated up again with a vacuum being
25 created in the second processing tool. In the latter case, the
homoepitaxial portion of the temporary heteroepitaxial film
30 15 serves as a protective coating over the monolayer portion of
the heteroepitaxial film during such transit between separate
processing tools.

35 In that the atomic diameter of barium is 4.48 Å, and that
of strontium is 4.29 Å, it can be appreciated how the
20 formation of a monolayer of these metal atoms, for example, on
40 a substrate by the techniques presented herein permits the
formation of an extremely thin, yet effective diffusion
barrier.

45 While not desiring to be bound to any particular theory,
25 it nonetheless is thought that the underlying mechanism by
which the metal monolayer prevents diffusion of the copper, or
50 other highly diffusive metal, through the barrier layer into

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5 the semiconductor or insulating substrate is at least in part
attributable to the fact that metal atoms are provided in the
10 monolayer which have relatively large electron clouds which can
overlap or touch each other between the metal atoms to
5 effectively form an energy barrier against movement of copper
15 atoms therethrough. As will be understood by one of ordinary
skill in the art, from a standpoint of terminology, the
20 electron clouds are also spoken of as atomic orbitals occupied
by electrons in different energy levels or shells, and the
10 electron cloud is a cloud of negative charge formed of
electrons of an electron density distribution corresponding to
25 the element at issue.

An important advantage of the invention is the ease with
which the diffusion barrier layer can be formed. Where metal
30 halides are used as a precursor in forming the diffusion
barrier film, the precursor, e.g., BaF₂ or SrF₂, can be
15 deposited for a sufficient duration of time to ensure complete
coverage of the silicon substrate. Such complete coverage can
35 be achieved within relatively short period of time, e.g., about
be achieved within relatively short period of time, e.g., about
20 one minute using MBE deposition of a metal halide on the
substrate, depending on deposition conditions. Also, the
40 length of deposition time is not critical provided it is at
least high enough to establish the diffusion barrier film;
45 deposition times of several minutes are not detrimental to the
procedure, and the deposition temperature also is not critical.
25 In the second step, all components of the precursor except for
50 the monolayer of metal atoms, are removed by the post-growth

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5 annealing procedure. The metal atoms of this thin layer adhere
tightly to the substrate, and consequently, the second step can
10 be carried out over a wide range of time and temperature
conditions without adversely affecting the formation and
5 character of the diffusion barrier layer.

15 By way of a specific illustration of forming a diffusion
barrier on a semiconductor substrate, BaF₂ can be used as the
20 barrier film precursor and a silicon wafer can be used as the
substrate. The silicon substrate first is deoxidized by vacuum
10 annealing at 900°C for one hour to remove the silicon dioxide
passivation layer. Then the substrate can be brought to a
25 deposition temperature of 750°C in a VG Semicon V80H MBE growth
chamber at a vacuum of less than 1×10^{-10} mbar. All temperature
measurements are made from a noncontact thermocouple gauge. A
30 15 BaF₂ effusion cell can be heated to 1050°C. While the
substrate holder is mechanically rotated, an electron beam from
a RHEED diagnostic system is directed toward the substrate.
35 The beam is focused until the RHEED pattern of a single crystal
silicon surface appears on the RHEED screen. The shutters in
20 front of the substrate holder and the effusion cell are then
40 opened to allow BaF₂ molecules to impinge on the substrate
surface. Deposition of BaF₂ is allowed to continue until the
single crystal silicon RHEED pattern disappeared and is
45 replaced by a single crystal BaF₂ pattern. Deposition is then
25 halted by closing the substrate and effusion source shutters.
The substrate temperature is then raised to 800°C and held
50 until a RHEED pattern similar to that of the single crystal

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5 silicon substrate reappears. It will be understood that the
above-provided exemplary protocol is provided merely for sake
10 of illustration, and not limitation.

In the mode of the invention being discussed above in
5 which metal halides are used as precursor compound for forming
the diffusion barrier film, the precursor compounds that can be
15 used include, for example, BaF₂, BaCl₂, SrF₂, SrCl₂, CsF₁, CsCl,
RbF, and RbCl, and the like. Especially preferred are those
20 metal halide salts that have cubic halide, e.g. a cubic
fluorite, crystal structure. While not desiring to be limited
10 to any particular theory at this point, applicants nonetheless
consider that precursor compounds obtainable as metal halides,
25 e.g., BaF₂, BaCl₂, SrF₂, SrCl₂, CsF₁, CsCl, RbF, and RbCl, and
the like, that have cubic crystal structure will tend to
30 provide sources of metal atoms that are amenable to the above-
discussed decomposition reaction and interaction with the
silicon surface under readily implementable MBE and annealing
35 processing conditions. Although not desiring to categorically
exclude all metal halide salts having rutile crystal structure,
20 rutile metal halide salts may not be suitable for many
40 processing environments as they do not normally decompose under
typical MBE conditions.

In another mode of the invention for forming the diffusion
45 barrier film, the monolayer of metal atoms alternatively can be
25 formed in a one step operation (i.e., without a post-growth
anneal step) by directly depositing an elemental form of the
50 metal atoms, such as barium, via MBE on the surface of the

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-24-

10 semiconductor substrate. Since certain elemental metals such as
15 barium are highly reactive, appropriate precautions have to be
20 taken to handle, maintain and process the elemental barium in
25 an inert environment, e.g., under an argon gas atmosphere, up
30 until it is deposited upon the semiconductor.

35 Also, in another embodiment of this invention, it is
40 possible to form the monolayer of metal atoms directly on the
45 semiconductor substrate by the above-described two-step
50 decomposition reaction process involving a metal halide (i.e.,
MBE deposit/post-growth anneal), and then to increase the
thickness of the diffusion barrier film by depositing one or
more additional monolayers of metal atoms on the original
monolayer through depositing the elemental form of the metal
atoms, such as barium, via MBE on the original monolayer. That
is, while formation of a single monolayer on the substrate as
described above is sufficient to meet the diffusion barrier
objectives of this invention, it is also within the scope of
this invention to form one or more additional monolayers of the
metal on the original monolayer as long as the overarching
objective of forming a diffusion layer of extremely small
thickness is maintained. For example, the metal atom can be
deposited from an elemental form via MBE on the surface of the
silicon substrate. In this way, a plurality of monolayers can
be formed as contiguous layers upon the substrate to form an
overall thickness in the diffusion barrier layer of any desired
thickness. Since thin thicknesses are desired, the diffusion
barrier preferably is built up to an overall thickness that

5 -25-

does not exceed 100Å, and more preferably does not exceed 20Å.
FIG. 7A illustrates this scenario in which a plurality of
monolayers 71a, 71b, and 71c are sequentially formed, upon the
surface 72 of substrate 73, one on the other, in the manners
described above. Then, a conductor material or other material
(not shown) can be formed over the outermost monolayer 71c. In
this embodiment, each of monolayers 71a, 71b, and 71c are
formed of the same type of metal atoms, and together, they form
the barrier film. Also, while three monolayers are depicted in
FIG. 7A, the plurality of monolayers can be two or more.

Also, it is possible to deposit a combination of different
types of metal atoms during precursor deposition on a substrate
to form a composite diffusion barrier monolayer. For example,
because the melting and sublimation temperatures of strontium
fluoride and barium fluoride are similar, the temperature
ranges for MBE deposition of a strontium fluoride precursor
onto silicon and for the evaporation of the strontium fluoride
precursor from silicon almost completely overlap those given
above for barium fluoride. Thus, temperatures in the mid-
portion of the ranges given for barium fluoride on silicon are
also satisfactory for the MBE deposition and evaporation of
strontium fluoride. However, the temperatures required to
sublimate, i.e., directly change the state of the source solid
crystal form to a gas for deposition via MBE, for barium
fluoride and strontium fluoride are slightly different.
Consequently, to control the ratio of barium to strontium in a
composite monolayer of a barrier layer to be formed, the barium

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fluoride and strontium fluoride should be deposited using
separate effusion cells for the MBE chamber. In any event, a
composite monolayer can be formed of barium and strontium atoms
in this manner. FIG. 7B illustrates this embodiment of the
5 invention where the barrier film is a composite monolayer 71
formed of different types of metal atoms 71d and 71e. Two or
15 more different types of metal atoms can be provided in the
composite monolayer 71. Then, a conductor material or other
material (not shown) can be formed over the composite monolayer
20 71.

Also, if an additional monolayer or monolayers are
25 deposited on the original monolayer formed on the surface of
the substrate, the different monolayers can have the same or
different types of metal atoms by appropriate selection of the
30 precursor compounds at the different stages of processing. For
instance, as illustrated in FIG. 7C, the barrier film is
15 comprised of a plurality of contiguous monolayers 71f, 71g and
71h in which different monolayers thereof are formed of
35 different types of metal atoms. In this illustration, layers
40 71f and 71h are formed of the same type of metal atoms while
intervening monolayer 71g is formed of a metal atom that is
45 different from the metal atoms in layers 71g and 71h. However,
there is no requirement that barrier film arrangements with
50 three or more monolayers containing the different types of
25 metal atoms must alternate through the stack of monolayers in
any particular pattern. Also, while three monolayers are
depicted in FIG. 7C, the embodiment is not limited to that

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5

plural number. Also, composite monolayers, such as described in
FIG. 7B can be used in combination with one or more contiguous
10 monolayers formed thereon having a single type of metal atoms,
such as shown in FIG. 7A, or different types of metal atoms in
5 different respective monolayers, such as illustrated in FIG.
15 7C.

As yet another mode of applying the metal halide precursor
to the substrate to form the temporary heteroepitaxial film,
20 r.f. sputtering, such as depicted in FIG. 6, can be used. In a
10 sputtering chamber 36, an argon-ion gun 38 directs a beam 40
onto a supply (target) 42 of barium fluoride, for example,
25 causing deposition of barium fluoride onto a substrate 44 by
sputtering. Here, as in the case of MBE deposition, the post-
growth annealing of the substrate can take place within the
30 15 sputtering chamber in order to remove BaF₂ molecules and the
fluorine atoms leaving only a thin layer of barium atoms as a
monolayer adhering to the surface of the substrate. The
35 metallization (conductor) layer can also be applied to the
substrate while it is inside the sputtering chamber.

40

20 Sputtering can also be used to deposit a diffusion barrier of
other metal atoms, such as strontium atoms, in a similar
manner. Also, a combination of different types of metal atoms
45 could be sputtered in the same monolayer or in different
monolayers using different sputtering targets formed of
25 different respective metal halide precursors. In general,
however, MBE is superior to r.f. sputtering because sputtering
50 can cause dissociation of the barium-fluorine bond before the

55

5 -28-

5 barium fluoride molecule reaches the substrate surface which
facilitates the formation of the temporary heteroepitaxial
10 film.

10 As other different modes for forming the diffusion barrier
5 film on a substrate, deposition processes other than MBE and
r.f. sputtering can be used, for example, physical and chemical
15 vapor deposition, wet chemical processes, and liquid phase
vapor deposition, wet chemical processes, and liquid phase
epitaxy. For instance, precursors used in metal-organic
20 chemical vapor deposition (MOCVD) to form the diffusion barrier
on a semiconductor or insulating substrate include Ba (2,2,6,6-
10 tetramethyl-3,5 heptanedionate) and Sr (2,4-pentanedionate).

25 As illustrated in FIG. 8, the diffusion barrier produced
in accordance with the invention can be used not only to
prevent diffusion of conductor metals into a semiconductor
30 substrate, but also to prevent diffusion of the conductor metal
into an insulating layer. In FIG. 8, layer 46 is a
15 semiconducting substrate, for example, a semiconducting layer of
silicon, and layer 48, which overlies layer 46, is an
35 insulating layer of silicon dioxide (SiO_2). A plug 45 of a
semiconductor substrate, for example, a semiconducting layer of
40 silicon, and layer 48, which overlies layer 46, is an
insulating layer of silicon dioxide (SiO_2). A plug 45 of a
15 metal, such as copper, is located in a via hole through
insulating layer 48, and makes ohmic contact with the
45 semiconducting layer 46 through a thin diffusion barrier layer
47 of barium formed by one of the processes described above.
This plug is used to conduct current between layer 46 and
50 another layer (not shown) which is separated from layer 46 by
insulating layer 48. In the same process, the sidewall of the
via hole is lined with a barium diffusion barrier 49, which

5 -29-

5 prevents diffusion of the copper into the insulating layer.
The barium or strontium atoms are deposited onto an insulating
10 layer in the same way in which they are deposited onto silicon.

15 As will be apparent from FIG. 8, the minimization of the
thickness of the side wall diffusion barrier 49 makes it
possible to use copper for interconnections between layers.
The copper interconnects can be significantly narrower than
20 tungsten interconnects having the same current capacity, and
the diffusion barrier is also very thin. Therefore the use of
25 the diffusion barrier in accordance with the invention as a
liner for via holes in insulating layers, can contribute
significantly to the minimization of the lateral dimensions of
an integrated circuit of which the elements shown in FIG. 8 are
30 a part. Because the diffusion barrier 49 is very thin, it
permits the use of via holes of relatively low aspect ratio,
making them easier to fill with conducting metal and
eliminating voids which result in failures or rejection of ICs.

35 It will be understood that this invention is not limited
to the above-illustrated substrate materials, conductor
40 materials, and materials used to make the diffusion barrier, as
long as other criterion understood and set forth herein for
these respective materials are satisfied.

45 For instance, the material used for forming the diffusion
barrier can be any appropriate metal in elemental form or
50 precursor molecular compound from which a layer of metal atoms
(i.e., a monolayer) can be formed on a semiconductor or
insulating substrate.

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5 The substrate material upon which the diffusion barrier is
formed is not particularly limited and can include
10 semiconductor materials and insulating materials used in
semiconductor device fabrications. The semiconductor material
5 can be, for example, Si, Ge, InP, GaAs, SiC, GaN, AlN, InSb,
15 PbTe, CdTe, HgTe, Hg₂Cd_{1-x}Te, PbSe, PbS, and tertiary
combinations of these materials. The semiconductor material can
be monocrystalline or polycrystalline. The semiconductor
20 substrate can be in bulk wafer form, deposited or grown layer
10 form (e.g., epitaxially grown), or silicon-on-insulator (SOI)
form. The semiconductor can be doped or undoped with impurities
25 (e.g., p-, n-doping). The insulating substrate material can be,
for example, SiO_x, SiO₂, BaF₂, SrF₂, CaF₂, silicon nitride, PSG,
or BPSG. For example, a thin diffusion barrier film formed of
30 15 a barium, strontium or cesium monolayer (or monolayers) can be
used to line via holes in insulators made of BaF₂, SrF₂, and
CaF₂.

35 As to the types of conductor materials that can be formed
on the diffusion barrier, these include conventional metals and
40 20 metal alloys used for wiring line, interconnects, bonding pads,
and so forth, in semiconductor device or opto-electronic device
fabrication. The present invention is especially useful for
45 providing an *in situ* barrier to electrically conductive metals
which tend to diffuse into semiconductor and insulating
50 25 materials common to semiconductor processing. These conductive
metals include, for example, pure copper, copper alloys (e.g.,
Cu-Al, Cu-Si-Al), copper doped with a dopant (e.g., aluminum)

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5 that impedes electromigration, gold, silver, or platinum. In
the case of copper, it may be desirable to alloy it with small
10 percentages (e.g., < 5%) of other metallic substances to
prevent electromigration. The conductor material can be
5 deposited on the diffusion barrier by any conventional
15 technique, including, e.g., electroplating, electroless
deposition, sputtering, chemical vapor deposition, e-beam
20 evaporation, and so forth. For example, copper can be deposited
by e-beam evaporation at 1×10^{-9} millibars in a heated chamber,
10 or at 10×10^{-11} millibars under a nitrogen environment. The
conductor film can be patterned on the diffusion barrier by
25 various techniques, such as by conventional additive or
subtractive processes known and used in semiconductor
processing (e.g., photolithographic processing). The invention
30 15 can also be used to prevent diffusion of gallium and/or arsenic
from gallium arsenide into silicon and other substrates.

A number of advantages and improvements are achieved by
35 the present invention which can be exploited in the
semiconductor device processing industry. A principal advantage
20 of this invention is that the thickness of the diffusion
40 barrier layer can be made extremely thin. In practice,
depending on the surface characteristics of the substrate
material onto which the diffusion barrier layer is deposited,
45 the thickness of the diffusion barrier layer according to this
25 invention will generally be formed in the range of
50 approximately 5 Å to 100 Å. In the case of a smooth, highly
planarized substrate material, e.g., a substrate having a

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5 surface roughness well below 5Å, the diffusion barrier can be
made as thin as one monolayer, which will have a thickness
10 slightly less than 5 Å corresponding the atomic diameter of
the metal atoms forming the diffusion barrier. For such smooth
5 substrates, the diffusion barrier formed of one monolayer
15 having a thickness less than 5Å in thickness will
satisfactorily inhibit diffusion of copper and other conductors
into the substrate. With substrate materials having a
20 relatively greater surface roughness, the thickness of the
10 diffusion barrier layer will tend to vary. For instance, the
diffusion barrier layer on a substrate having a surface
25 roughness greater than 5Å may be formed so as to have a
thickness value in the range of approximately 5 to 100 Å, with
metal atoms of the diffusion barrier layer accumulating at any
30 15 step edges on the substrate surface. Thus, the diffusion
barrier film of this invention is only one monolayer or a
multiple number of contiguous monolayers formed on the
35 substrate surface, and in any event, it need not be more than
approximately 100Å in total thickness to achieve the objectives
20 of this invention for current and future anticipated
40 semiconductor device fabrication specifications. A large scale
integrated circuit having copper conductors and a diffusion
barrier film according to this invention with a thickness in
45 the range of approximately 5Å to approximately 100Å, can
25 achieve an extremely high component density, which reduces the
number of layers required for a given number of components, and
50 very low heat dissipation. In the practice of this invention,

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therefore, the diffusion barrier thickness can vary from a
thickness less than about 5Å to a greater thickness, which can
be up to about 100Å, preferably up to no more than 20Å.

10 Conventional alternative diffusion barriers are significantly
5 thicker than 100Å.

15 Another advantage of the invention is that the diffusion
barrier film, where it is barium or strontium, or a similar
metal, is compliant, i.e., it is mechanically soft and easily
20 deformable. The compliance of the diffusion barrier film allows
10 dissimilar materials to be put together without introducing
defects, such as voids or mechanical stresses, at the interface
which may have detrimental effects on device performance, the
25 diffusion barrier film, or the metallization layer.

Furthermore, barium and strontium, or like metals, can form
30 15 intermetallic compounds with copper ($BaCu_{1-x}$ and Cu_xSr are
examples), causing copper atoms to be tightly bound to the
barium or strontium at the interface and unable to migrate past
35 the barium or strontium layer into the silicon.

Also, while the barrier film based on one or more
20 monolayers of metal atoms that is used in this invention has
40 been illustrated herein specifically as a barrier to diffusion
of metal conductors into substrate materials, it will be
understood that the barrier film is not necessarily limited to
45 that use alone, as it possesses many advantageous attributes
25 that could be exploited in semiconductor device fabrications.
For example, the barrier film could be used as a barrier layer
50 in the fabrication of semiconductor laser devices, such as

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those having heterojunctions and incorporating different semiconductor materials, e.g., GaAs on top of silicon.

10 While the invention has been shown and described with reference to certain preferred embodiments, it will be

5 understood by those skilled in the art that changes in form and detail may be made without departing from the spirit and scope
15 of the appended claims.

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Claims

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-35-Claims

10 1. A semiconductor device, comprising:
a substrate (18), a barrier film (24) on the substrate
(18), a material (22) directly on the barrier film (24);
5 characterized in that the barrier film (24) includes a
monolayer on the substrate (18).
15

20 2. A semiconductor device according to claim 1, wherein the
barrier film (24) has a thickness less than 100Å.

10 3. A semiconductor device according to claim 1, wherein the
barrier film (24) has a thickness less than 20Å.
25

30 4. A semiconductor device according to claim 1, wherein the
15 monolayer of the barium film (24) comprises metal atoms
selected from barium atoms, strontium atoms, cesium atoms, and
rubidium atoms, singly or in combinations thereof, located on
35 said surface of said substrate (18).

20 5. A semiconductor device according to claim 1, wherein the
40 barrier film (24) comprises a plurality contiguous monolayers
(71a-c) of metal atoms located on the surface of the substrate
material (18).
45

25 6. A semiconductor device according to claim 1, wherein the
50 barrier film (24) comprises a plurality of contiguous
monolayers comprising two or more different types of metal

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atoms selected from the group consisting of barium atoms,
strontium atoms, cesium atoms, and rubidium atoms, located on
said surface of said substrate (18).

10

5 7. A semiconductor device comprising:

15 a substrate (18) having a surface, a barrier film (24) on
the substrate (18), a material (22) directly on the barrier
film (24);

20 and characterized in that the barrier film (24) is

10 comprised of a layer of elemental metal atoms attached to said
surface.

25

8. A semiconductor device comprising:

30 a substrate (18), a barrier film (24) on the substrate
15 (18), a material (22) directly on the barrier film (24);
and characterized in that the barrier film (24) has a
thickness less than 100Å.

35

9. A semiconductor device comprising:

40 20 a substrate material (18) having a surface, a barrier film
(24) on the substrate surface, a conductor (22) directly on the
barrier film (24), and the conductor (22) having a tendency to
45 diffuse into the substrate material (18) if in direct contact
therewith;

50

25 characterized in that the barrier film (24) has a layer
comprising elemental metal atoms attached to the substrate
surface surface, and wherein the barrier film layer (24)

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comprising elemental metal atoms serves as a barrier,
inhibiting diffusion of the conductor (22) into the substrate
material (18).

10

5 10. A semiconductor device according to claim 9, wherein the
barrier film (24) has a thickness of not more than
15 approximately 100Å.

20

10 11. A semiconductor device according to claim 9, wherein the
barrier film (24) has a thickness of not more than
approximate 20Å.

25

15 12. A semiconductor device according to claim 9, wherein the
barrier film (24) has a thickness of not more than
approximately 5Å.

35

13. A semiconductor device according to claim 9, wherein the
monolayer of the barium film (24) comprises metal atoms
selected from barium atoms, strontium atoms, cesium atoms, and
20 rubidium atoms, singly or in combinations thereof, located on
40 said surface of the substrate (18).

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14. A semiconductor device according to claim 9, wherein the
barrier film (24) comprises a plurality contiguous monolayers
25 (71a-c) of metal atoms located on the surface of the substrate
material (18).

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10 15. A semiconductor device according to claim 9, wherein the barrier film (24) comprises a plurality of contiguous monolayers comprising two or more different types of metal atoms selected from the group consisting of barium atoms, 5 strontium atoms, cesium atoms, and rubidium atoms.

15 16. A semiconductor device according to claim 9, wherein said barrier film (24) is a single monolayer attached to said surface of the substrate material (18).

20 10 17. A semiconductor device according to claim 9, in which said substrate material (18) is a semiconductor.

25 15 18. A semiconductor device according to claim 9, in which said substrate material (18) is a silicon semiconductor.

30 35 19. A semiconductor device according to claim 9, in which said substrate material (18) is an insulating material.

40 20 20. A semiconductor device according to claim 9, in which said substrate material (18) is silicon oxide.

45 21. A semiconductor device according to claim 9, in which the conductor (22) is a metal.

50 25 22. A semiconductor device according to claim 9, in which the conductor (22) comprises copper.

5

23. A process for making a semiconductor device characterized
10 by the steps of:

5 forming, on a surface (51) of a substrate material (52), a
barrier film (54) having a monolayer of metal atoms immediately
15 adjacent the surface (51) of the substrate material (52); and
depositing a material (22) directly on the barrier film
20 (54).

20

10 24. A process for making a semiconductor device characterized
by the steps of:

25 forming, on a surface (51) of a substrate material (52), a
barrier film (54) including a layer of elemental metal atoms
attached to said surface (51), and where the barrier film has a
30 15 thickness of less than 100Å; and
depositing a material (22) directly on the barrier film
(54).

35

20 25. A process according to claim 24, where the substrate
material (52) is selected as silicon and the material (22) is
40 selected as a conductor material.

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26. A process according to claim 25, wherein the conductor
material (22) comprises copper.

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27. A process according to claim 24, wherein the barrier film
(54) has a thickness of not more than approximately 20Å.

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28. A process according to claim 24, wherein the barrier film (54) has a thickness of not more than approximately 5Å.

10

29. A process according to claim 24, wherein the barrier film (54) comprises one or more monolayers of metal atoms.

15

30. A process according to claim 24, wherein said step of forming said barrier film (54) comprises sequentially forming a plurality of contiguous monolayers (71a-c) of metal atoms on 10 said surface (51) of said substrate material (52).

25

31. A process according to claim 24, in which the step of forming the barrier film (54) comprises depositing a monolayer precursor compound (50) on the substrate (52) by molecular beam epitaxy, and then annealing the monolayer precursor compound to form a monolayer (54) of metal atoms on the surface (51) of the substrate (52).

35

32. A process according to claim 31, wherein the precursor compound (50) is a metal halide.

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33. A process according to claim 31, wherein the precursor compound (50) includes a Group I metal halide.

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34. A process according to claim 31, wherein the precursor compound (50) includes a Group II metal halide.

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35. A process according to claim 31, wherein the precursor
compound (50) is a metal halide selected from one or more of
BaF₂, BaCl₂, SrF₂, SrCl₂, CsF, CsCl, RbF, and RbCl.

5 36. A process according to claim 31, wherein the depositing
and annealing steps are repeated one or more times to form a
15 plurality of contiguous monolayers (71a-c) on the surface (51)
of the substrate (52).

20 10 37. A process according to claim 24, in which the step of
forming said barrier film (54) comprises depositing a monolayer
25 precursor compound (50) on said substrate (52) by sputtering,
and then annealing said monolayer precursor compound (50) to
form a monolayer (54) of metal atoms on the surface (51) of the
30 15 substrate (52).

35 38. A process according to claim 37, wherein the precursor
compound (50) is a metal halide.

40 20 39. A process according to claim 37, wherein the precursor
compound (50) includes a Group I metal halide.

45 40. A process according to claim 37, wherein the precursor
compound (50) includes a Group II metal halide.

25 50 41. A process according to claim 37, wherein the precursor
compound (50) is a metal halide selected from one or more of

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5 BaF₂, BaCl₂, SrF₂, SrCl₂, CsF, CsCl, RbF, and RbCl.

10 42. A process according to claim 37, wherein the depositing
and annealing steps are repeated one or more times to form a
5 plurality of contiguous monolayers (71a-c) on the surface (51)
15 of the substrate (52).

20 43. A process according to claim 24, in which the step of
forming said barrier film (54) comprises depositing a monolayer
10 precursor compound (50) on said substrate (52) by physical
vapor deposition, and then annealing said monolayer precursor
25 compound (50) to form a monolayer of metal atoms on the surface
(51) of the substrate (52).

30 15 44. A process according to claim 24, in which the step of
forming said barrier film (54) comprises depositing a monolayer
precursor compound (50) on said substrate (52) by a deposition
35 process selected from the group consisting of molecular beam
epitaxy and physical vapor deposition, and then chemical
20 etching said monolayer precursor compound (50) to form a
monolayer of metal atoms on the surface (51) of the substrate
40 (52).

45 45. A process according to claim 24, in which the substrate
25 material (52) is a semiconductor material.

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46. A process according to claim 24, in which the substrate material (52) is silicon semiconductor.

10 47. A process according to claim 24, in which the substrate
5 material (52) is an insulating material.

15 48. A process according to claim 24, in which the substrate material (52) is a silicon oxide.

20 10 49. A process according to claim 24, in which the conductor (22) is a metallic conductor.

25 50. A process according to claim 24, in which the conductor (22) comprises copper.

30 15 51. The product of the process as recited in claim 23.

35 52. The product of the process as recited in claim 24.

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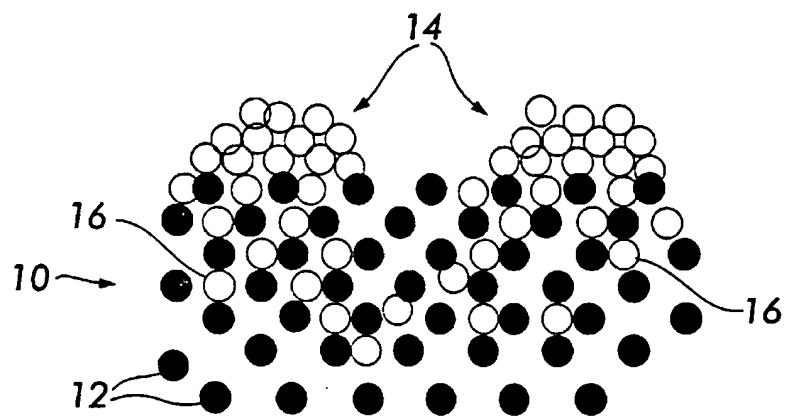
FIG. I

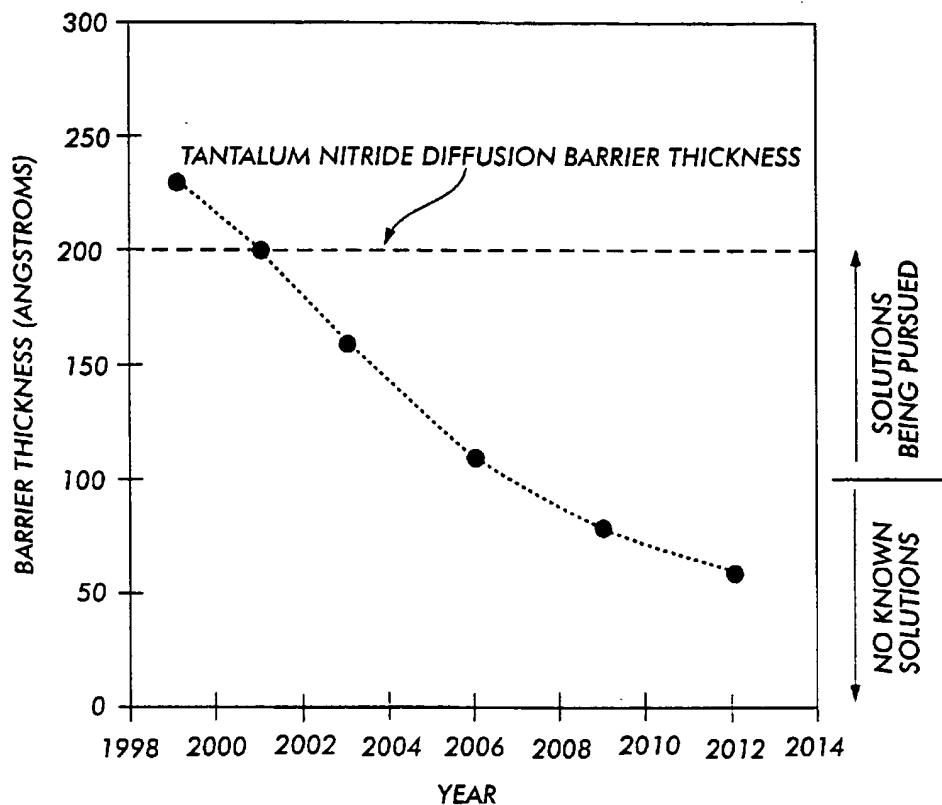
FIG.2

FIG.3

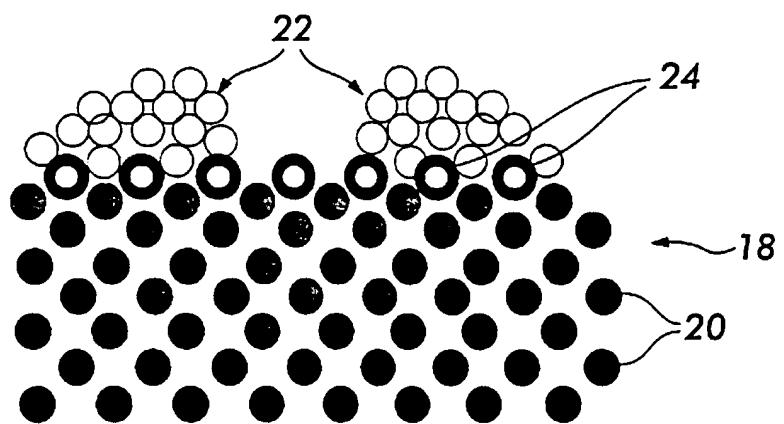


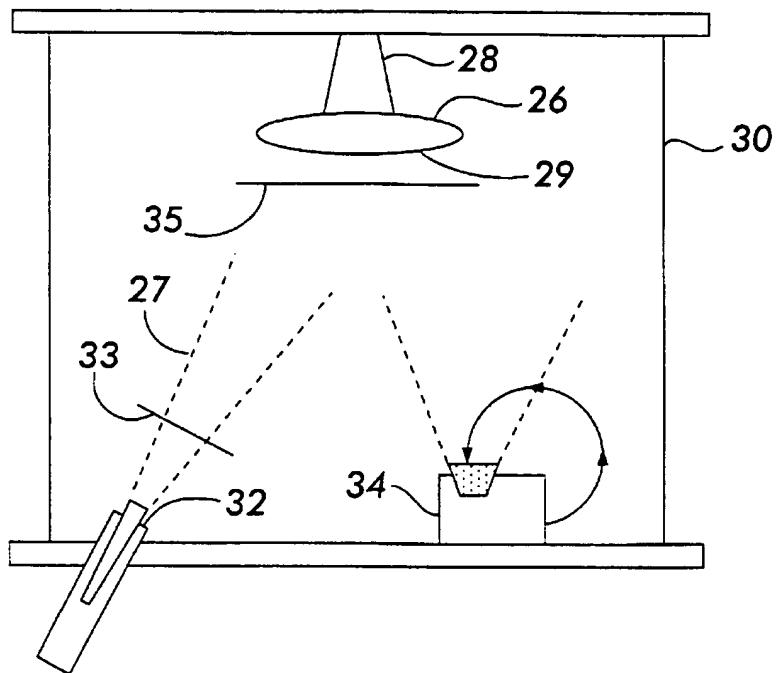
FIG.4

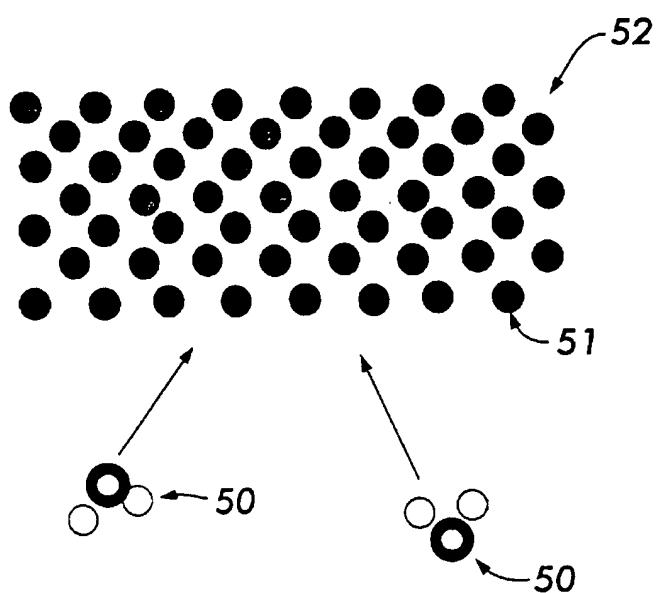
FIG. 5A

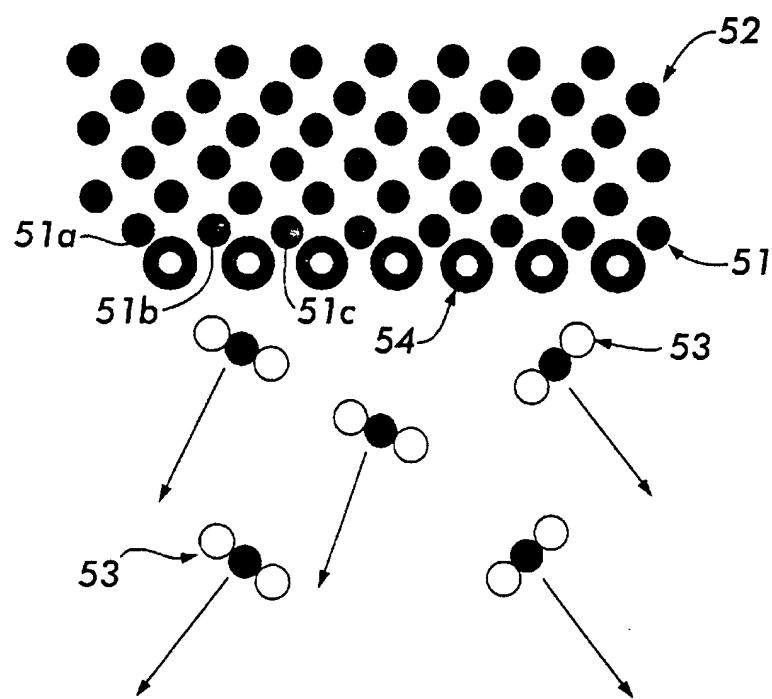
FIG. 5B

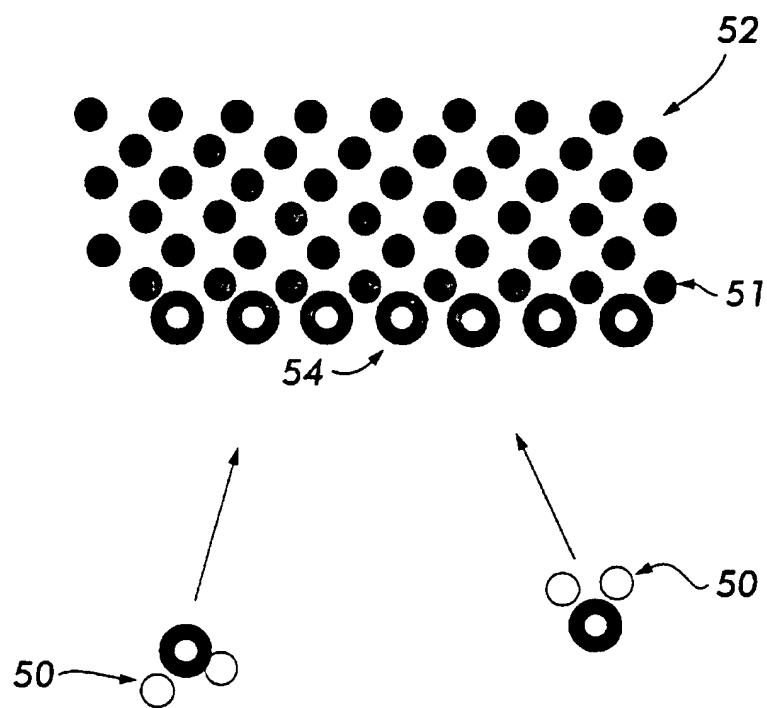
FIG.5C

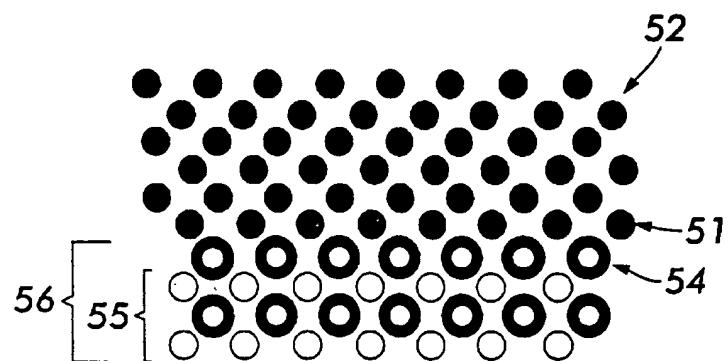
FIG. 5D

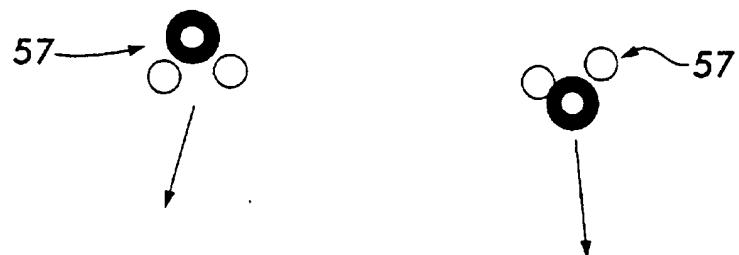
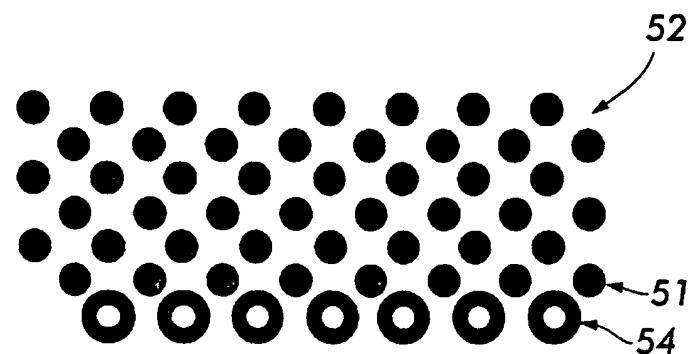
FIG. 5E

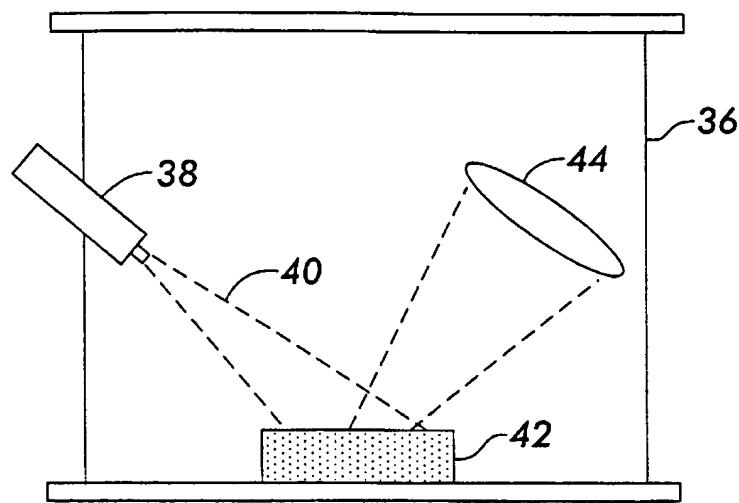
FIG.6

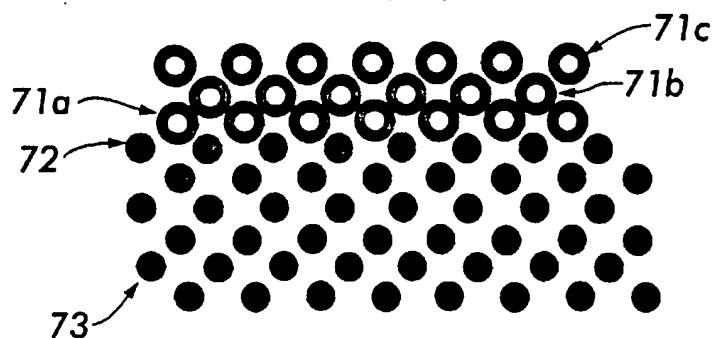
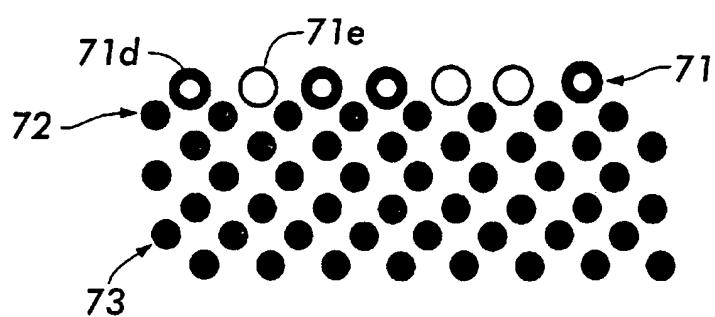
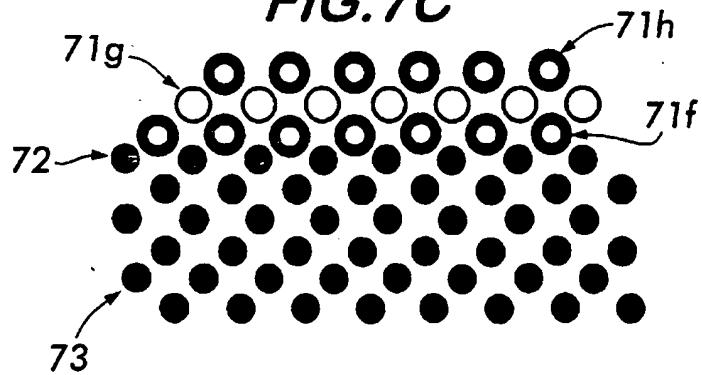
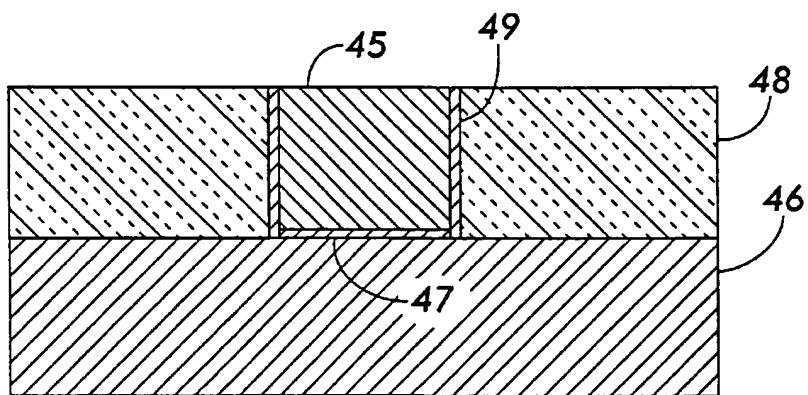
FIG. 7A**FIG. 7B****FIG. 7C**

FIG.8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/16719

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(6) :H01L 29/43, 21/441 US CL : 438/687, 643; 257/762,767 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) U.S. : 438/687, 643; 257/762,767		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) NONE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 6 310 509 A (NONE) 04 NOVEMBER 1994, (04/11/94) abstract	1, 5, 7, 9., 14, 17-23, 51
X	EP 0 851 483 A (CHEN et al) 01 JULY 1998, (01/07/98) p.4, lines 55-59; p. 5, lines 1 and 15-19.	1, 2, 5, 7-10, 14, 17-26, 29-30, 45- 52
X	US 5,637,533 A (CHOI) 10 JUNE 1997, (10/07/97) col. 2, lines 24-51.	1, 2, 5, 7, 9, 14, 17-23, 51
X	US 5,670,420 A (CHOI) 23 SEPTEMBER 1997, (23/09/97) col. 1, lines 63068; col. 2, lines 10-28.	1, 2, 7, 9, 14, 17-24, 51
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier document published on or after the international filing date "C" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "D" document referring to an oral disclosure, use, exhibition or other means "E" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 30 OCTOBER 1999	Date of mailing of the international search report 17 NOV 1999	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CARIDAD EVERHART Telephone No. (703) 308-0956	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/16719

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	EP 0 881 673 A (ASHLEY, et al) 02 DECEMBER 1998, (02/12/98) col. 8, lines 55-59; col. 9, lines 1-35.	1, 2, 5, 7-10, 17- 24, 45-52
X, P	US 5,824,599 A (SCHACHAM-DIAMAND et al) 20 OCTOBER 1998, (20/10/98) col. 6, lines 35-50	1, 5, 7, 9, 14, 17, 23, 51